Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Quantitative Determination of Total Cesium in Savannah River Site (SRS) Tank Waste by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES)

Project highlight.

Utilization of the significant and unique wavelength dynamic range (165 to 1100 nm) available on the Leeman Prodigy Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) allows for quantification of cesium using the emission line 894.347 nm (Figure 1) without the potential of Barium interference in nuclear waste samples. Samples are added to a Sodium Peroxide Fusion and Lithium Carbonate buffer in 2% nitric acid solution to increase sensitivity of the easily ionizable (<6 eV) cesium for quantitation to 5 pbb. Through direct comparison of analytical data results, the method is proven to be complementary to the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis (LOQ 100 ppt) in support of the Department of Energy's (DOE) Nuclear Waste Mission.

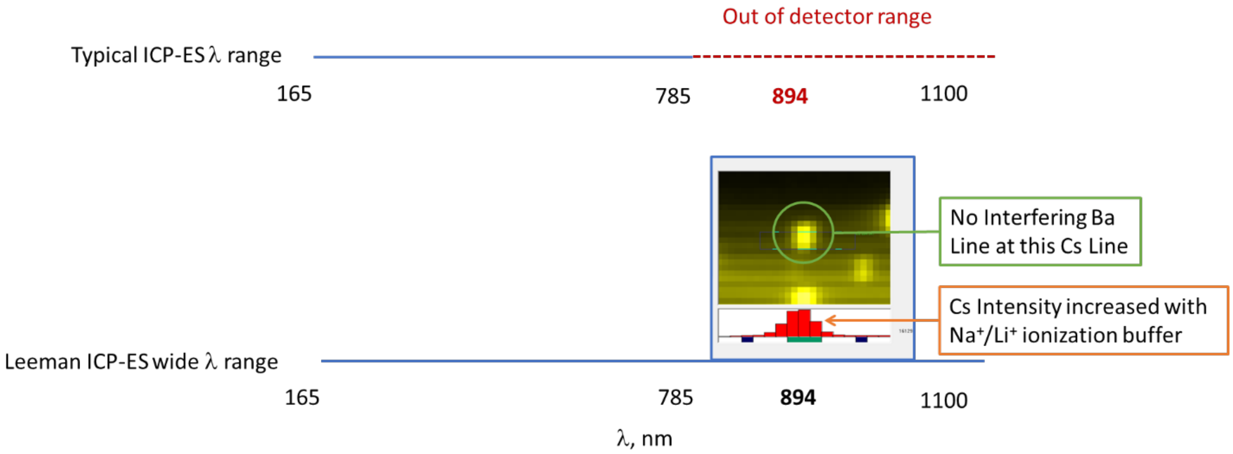


Figure 1. Echelle image of low level Cs 894.347 nm on Leeman Prodigy ICP-ES with wide dynamic range.

Awards and Recognition

Not Applicable

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

Signature **Date**

Quantitative Determination of Total Cesium in SRS Tank Waste by Inductively Coupled Plasma Emission Spectroscopy

Project Team: Nathan Wyeth (Primary), Mark Jones, Thomas White, and Charles Coleman

Subcontractor: Not Applicable

Project Type: Seedling

Project Start Date: April 1, 2020
Project End Date: September 30, 2020

The analysis of cesium (Cs) is fundamental for waste characterization and source identification of fission products in nuclear waste remediation and in non-radioactive simulant tests to support tank closure programs. Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) has not been utilized for total Cs determinations in the past due to the inability for quantitative determination below sub-parts per million (ppm) levels and spectroscopic interferences. Currently, Cs isotopic analysis for tank waste at SRS is performed by Inductively Coupled Mass Spectrometry (ICP-MS) to ppt concentrations. However, total Cs by ICPMS faces the problem of isobaric interferences of some Cs isotopes by barium ions when present in samples and leads to bias high quantitation. Utilization of the expanded wavelength detection range of the Leeman Prodigy ICP-ES in combination with an ionization buffer (IB) results in a significant increase in spectral intensity without the impact of potential Ba interference when present in sample. This technique increased the sensitivity of ICP-ES from low ppm concentrations to low ppb concentrations.

FY2020 Objectives

- Evaluate ICP-ES Cs emission signal at wavelength 894.347 nm
- Establish Calibration with a minimum R^2 of 0.999
- Determine LOQ and evaluate methods to increase sensitivity
- Analysis of real SRS tank waste and simulant samples
- Data evaluation and direct comparison to ICP-MS
- Submission for publishing FY20

Introduction

The quantitative determination of cesium (Cs) by Inductively Coupled Emission Spectroscopy (ICP-ES) was performed at the Savannah River National Laboratory (SRNL) on both a non-radiological and a contained radiological Leeman Prodigy ICP-ES. The analysis of Cs at the Savannah River Site (SRS) is fundamental for waste characterization and source identification of fission products in nuclear waste remediation. In addition, Cs measurements in non-radioactive simulant tests are also essential to support the development of tank closure programs. SRNL utilizes Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for isotopic analysis of 133Cs (stable) and the 134Cs ($t_{1/2}$ = 2 y), 135Cs ($t_{1/2}$ = 2.3 x 10^6 y and 137Cs ($t_{1/2}$ = 30 y) radioisotopes. In samples containing barium ion daughter isotopes, Cs isotopic analysis is subject to isobaric interferences (e.g., 134Ba, 135Ba and 137Ba).

ICP-ES is not a technique utilized due to the inability for quantitative determination below sub-parts per million (ppm) levels (e.g., Cs 455.531 nm) and spectroscopic interferences (e.g., Cs 852.120 nm)[1] on standard ICP-ES systems due to detector wavelength (λ) range limitations (e.g., 165 nm to 785 nm). Sensitivity issues stem from the low ionization potential of Cs at 3.893eV and spectroscopic interferences with Argon (Ar) creating complex challenges for elemental Cs by this method[1].

The Leeman Prodigy ICP-ES was selected due to its wavelength detection range of 165 - 1100 nm[2]. The utilization of Cs emission line 894.347 nm in Axial mode provides a sensitive wavelength and a strong gaussian signal in comparison to line 455.531 nm (Figure 2). The line 894.347 nm is visible due to the instruments Large Format Programmable Array Detector (L-PAD) [2]. Additionally, an ionization buffer (IB) solution composed of a Sodium Peroxide Fusion (NaPF) solution and Lithium Carbonate (Li_2CO_3) in 2% nitric acid (HNO_3) is added to sample aliquots to increase line intensity. The goal is to lower the limit of quantitation (LOQ) from ppm concentrations to lower part-per billion (ppb) concentrations.

ICP-ES analysis of Cs was performed on real radiological Tank Closure Cesium Removal (TCCR) samples and Non radiological samples including a set of $CsGa_7O_{11}$ leaching samples. All ICP-ES analytical testing results were directly compared to ICP-MS for method validation of total Cs. Utilizing the ICP-ES can provide an accurate quantitative value for total Cs while providing a complementary technique to the current ICP-MS analysis for all groups and organizations performing Cs analysis for the Department of Energy's (DOE) Nuclear Waste Mission.

Approach

The approach of the project was to determine the sensitivity of Cesium in Axial mode at 894.347 nm with the primary goal of achieving an LOQ of 50 ppb or less and a method uncertainty of 30% 2-sigma at the LOQ. Following detection of a strong gaussian peak of total Cs, the project utilizes other easily ionizable elements (EIE) as ionization buffers by utilizing ionization interference to increase the signal of Cs[3]. Ionization interference is a phenomenon which shows a change in emission intensity, causing the ionization equilibrium to shift, when coexisting elements include an EIE, such as Na, K, and Cs[3]. The effect is expected to boost the emission intensity and lower the overall detection limit to low ppb concentrations for a total Cs determination.

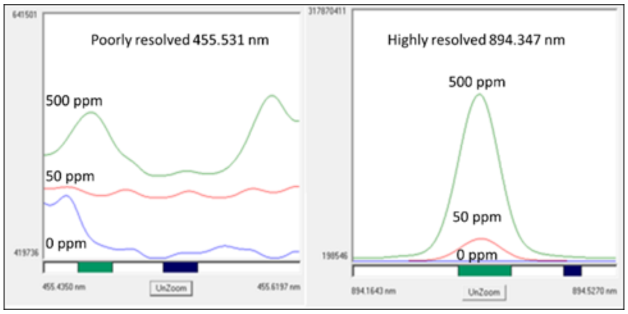
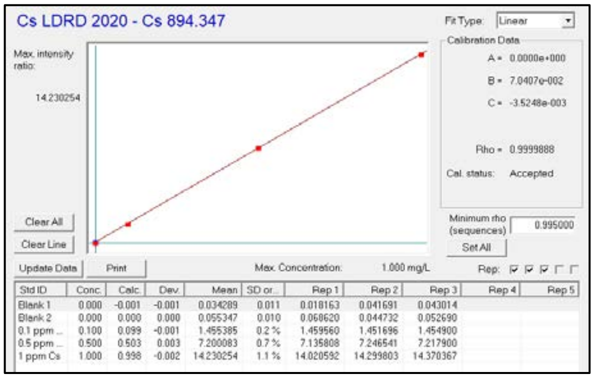


Figure 2. *Spectral overlay of Cs at 500 ppm, 50 ppm and Blank in Axial Mode. Emission line (Left) 455.531 nm, Emission line 894.347 nm(Right).*



Fit Type: Linear

Calibration Data

A = 0.0000e+000

B = 7.0407e-002

C = -3.5248e-003

Rho = 0.9999888

Cal. status: Accepted

Minimum rho (sequences) 0.995000

Max. Concentration: 1.000 mg/L

Rep: ☑ ☑ ☑ ☐ ☐

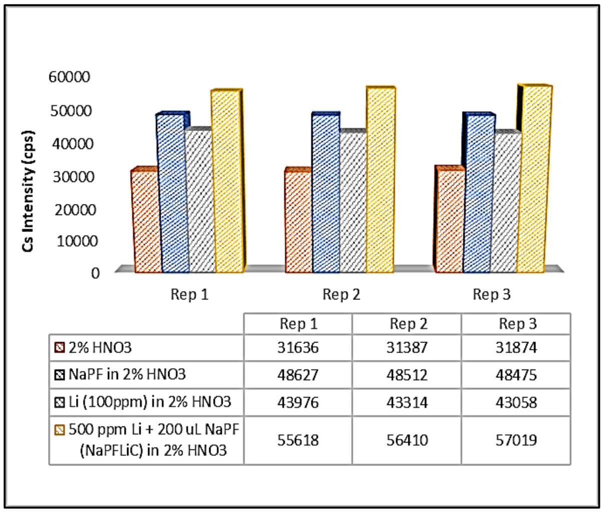
Std ID	Conc.	Calc.	Dev.	Mean	SD or...	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
Blank 1	0.000	-0.001	-0.001	0.034289	0.011	0.018163	0.041691	0.043014		
Blank 2	0.000	0.000	0.000	0.055347	0.010	0.068620	0.044732	0.052690		
0.1 ppm ...	0.100	0.099	-0.001	1.455385	0.2 %	1.459560	1.451696	1.454900		
0.5 ppm ...	0.500	0.503	0.003	7.200083	0.7 %	7.135808	7.246541	7.217900		
1 ppm Cs	1.000	0.998	-0.002	14.230254	1.1 %	14.020592	14.299803	14.370367		

Figure 3. *4 point linear Cs 894.347 nm calibration with an R^2 0.9999 from Blank, 100 ppb, 500 ppb and 1 ppm.*

The final approach is to establish a minimum linear calibration of R^2 0.999 (Figure 3) and perform Cs analysis on blanks, spiked samples at varying concentrations and real radiological/non-radiological samples from SRS nuclear waste mission. Only samples previously analyzed by ICP-MS are measured for total Cs, and the data sets are directly compared for accuracy, precision and method validation.

Results/Discussion

The IB for the method was chosen based on a measurement (n=3) of emission line 894.347 nm at 100 ppb of Cs in various matrices (Figure 4). The mixture of Li_2CO_3 and NaPF (NaPFLiC) resulted in a 56% increase in spectral intensity compared to a 2% HNO_3 matrix at 100 ppb. The NaPFLiC mixture was selected for further method development and sample analysis to provide a lower detection limit.



	Rep 1	Rep 2	Rep 3
▨ 2% HNO3	31636	31387	31874
▨ NaPF in 2% HNO3	48627	48512	48475
▨ Li (100ppm) in 2% HNO3	43976	43314	43058
▨ 500 ppm Li + 200 uL NaPF (NaPFLiC) in 2% HNO3	55618	56410	57019

Figure 4. *Effect of ionization buffer on 894.347 nm Cs spectral intensity at 100 ppb*

A limit of quantitation (LOQ), or minimum reporting limit, for the elemental wavelength set up on the Leeman Prodigy ICP-ES method was measured. All standards and blanks were prepared in 2% v/v Nitric Acid with the addition of 200 uL of NaPF, 1 mL of 5000 ppm Li_2CO_3, 50 uL of 400 ppm Indium (Internal Standard) for a total of 10 mL. After analyzing ten blanks, the LOQ was determined using

$$LOQ = 10 \times \sigma$$

where σ is the standard deviation of the ten blank measurements.

Table 1. Leeman Prodigy Cs Limit of Quantitation

Element/Line	Leeman Prodigy LOQ (mg/L)
Cs 894.347 nm	0.005

The limit of quantitation was determined to be 0.005 mg/L for Cs 894.347 nm (Table 1). An LOQ in 2% HNO_3 with a NaPF IB solution was determined at 0.022 mg/L, 4.4 times higher than with the NaPFLiC IB solution. The LOQ for Cs demonstrates excellent sensitivity on the ICP-ES.

Method uncertainties for the Cs 894.347 nm were measured to evaluate method sensitivity and accuracy. Ten preparations of quality control standards were prepared in 2% HNO3 with the NaPFLiC IB solution. 10 replicates were analyzed for Cs 894.347 nm at concentrations of 10 ppb. The uncertainty was calculated using

$$\text{2-sigma uncertainty} = [(\%RSD)^2 + (\%Bias)^2]^{1/2} \times 2$$

where the percent relative standard deviation (%RSD) is the standard deviation of the ten measurements divided by their mean times 100. The percent bias (%Bias) is the difference from the *true* value of the quality control standard, and the root sum of the squares (RSS) of the %RSD and %Bias was calculated and multiplied by 2 to obtain an uncertainty at 2-sigma. Table 2 lists the 2-sigma method uncertainty of Cs 894.347 nm at 10 ppb utilizing the NaPFLiC IB.

Table 2. Leeman Prodigy ICP-ES Uncertainty Determinations of Cs 894.347 nm utilizing NaPFLiC buffer.

Element/Line	**10 ppb 2-Sigma % Uncertainty Leeman Prodigy ICP-ES**
Cs 894.347 nm	10.7

A set of Non-Rad simulant TCCR samples from Crystalline Silicotitanate columns (CST), containing less than 5 ppm Na were analyzed at a 200x and 100x dilution utilizing the described method[4]. In addition, Table 3 shows a set of 16 samples from a $CsGa_7O_{11}$ leaching study that were analyzed for total Cs and compared to ICP-MS[5].

A set of various matrix SPK samples were also prepared and analyzed (Table 3) with a spike recovery within 10% of the expected value, further demonstrating method accuracy and precision. All results are less than 6% BIAS when compared to ICP-MS results except for the leaching study spike (SPK) data at less than 20% (Table 3).

Table 3. Cs analysis of Non-Rad TCCR simulants and $CaGa_7O_{11}$ samples via Leeman Prodigy ICP-ES utilizing NaPFLiC buffer.

Sample/DF	**Cs Matrix Spike mg/L**	**% Cs Spike Recovery**	**Cs ICP-ES (ug/g)**	**Cs ICP-MS (ug/g)**	**%BIAS**
Column A CST 200x			6037	6103	-1.1
Column B CST Top 200x			5359	5302	1.1
Column B CST Bottom 200x			4059	3993	1.6
Column C CST 200x			7486	7289	2.6
Column A CST 100x			6092	6103	-0.2
Column B CST Top 100x			5487	5302	3.4
Column B CST Bottom 100x			4124	3993	3.2
Column C CST 100x			7666	7289	4.9
Column A CST 200x + Cs Spk	0.15	-102	*5928	6103	-2.9
Column B CST Top 200x + Cs Spk	0.25	-98	*5377	5302	1.4
Column B CST Bottom 200x + Cs Spk	0.20	-110	*4097	3993	2.5
Column C CST 200x + Cs Spk	0.50	-106	*7689	7289	5.2
CGO-pH2-A-48hr 8x			2384	2490	-4.4
CGO-pH2-B-48hr 8x			2430	2520	-3.7
CGO-pH2-A-168hr 8x			2729	2790	-2.2
CGO-pH2-B-168hr 8x			2807	2890	-2.9
CGO-pH7-A-48hr 8x			1411	1440	-2.0
CGO-pH7-B-48hr 8x			1366	1390	-1.8
CGO-pH7-A-168hr 8x			1367	1420	-3.9
CGO-pH7-B-168hr 8x			1331	1360	-2.2
CGO-pH7-A-48hr 8x + Cs Spk	0.20	-109	*1745	1440	-17.5
CGO-pH7-B-48hr 8x + Cs Spk	0.20	-109	*1746	1390	-20.4
CGO-pH7-A-168hr 8x + Cs Spk	0.20	-109	*1740	1420	-18.4
CGO-pH7-B-168hr 8x + Cs Spk	0.20	-105	*1684	1360	-19.2

***denotes the SPK concentration minus total Cs value.**

Radiological TCCR samples from SRS Tank 10 Batch 3 were analyzed[6]. The samples contained ~1500 ppm of Na, demonstrating the buffer impact to sensitivity when high level Na is present in the sample (Table 4).

Table 4. Effect of IB on Cs in Rad Samples Containing High Levels of elemental Na.

Sample/DF	**Cs ICP-ES (ug/L) Li_2CO_3 Buffer**	**Cs ICP-ES (ug/L) NaPFLiC Buffer**	**Cs ICP-ES (ug/L) No Buffer**	**CS ICP-MS (ug/L)**	**%BIAS**
Tk 10 Batch 3 A-2 20x	508	540	**386**	**390**	*-1.0
Tk 10 Batch 3 A-1 20x	494	558	**378**	**390**	*-3.2

***denotes %BIAS compares no buffer ICP-ES to ICP-MS**

The use of an IB on samples with high Na content resulted in elevated values. These values were ~ 1.5 times the expected value indicating an additional increase in intensity due to the high levels of sodium. When the same samples were analyzed without the IB and measured against calibration containing the IB; the results were less than 3.5% BIAS from the ICP-MS results (Table 4).

A set of radiological TCCR teabag samples from Batch 3 were also analyzed for comparison to ICPMS[6]. The samples contained ~35 ppm of Na and were analyzed at a 5x dilution and resulted in a higher %BIAS at 13%.

Table 4. Cs Analysis of Radiological TCCR Teabag samples from Batch 3 utilizing NaPFLiC IB.

Sample/DF	**ICP-ES (ug/g)**	**ICP-MS (ug/g)**	**%BIAS**
Teabag A7 5x	1043	928	11.0
Teabag A8 5x	1038	911	12.3

To conclude sample testing, a 2 g/L Cs standard was analyzed by ICP-ES with IB to demonstrate linearity and method accuracy beyond the calibration range. The ICP-ES detected 1970 mg/L of Cs at a 100x dilution. The result is 1.5%BIAS from the *true* value of 2000 mg/L and a 7.1%BIAS from the ICP-MS value of 2110 mg/L.

Total Cs method has established accuracy, precision and an exceptionally low LOQ on the Leeman Prodigy ICP-ES. The method can provide an accurate quantitative value for total Cs while providing a complementary technique to the current ICP-MS analysis in support of Total Cs analysis for the Department of Energy's (DOE) Nuclear Waste Mission.

FY2020 Accomplishments

- Literature research and preliminary testing found that the Leeman Prodigy's extended wavelength range for detection could utilize wavelength 894.347 nm for a more sensitive Cs analysis which was not feasible with other ICP-ES systems due to detector limitations.
- An increase in spectral intensity, at 894.347 nm, greater than 50%, when utilizing a NaPFLiC IB compared to no IB.
- Calibration linearity was established at R^2 of 0.9999.
- LOQ was established at 5 ppb.
- Method uncertainty at 10 ppb is 10.7% 2-sigma.
- Total Cs analysis results of radiological and non-radiological samples were directly compared to ICP-MS data with a less than 15% BIAS across data sets, with the majority of samples tested less than 6% BIAS.

Future Directions

- Submission for publication

FY 2020 Peer-reviewed/Non-peer reviewed Publications

none

Presentations

none

References

1. Do V.K.; Yamamoto M.; Taguchi S.; Takamura Y.; Surugaya N.; Kuno T. *Quantitative determination of total cesium in highly active liquid waste by using liquid electrode plasma optical emission spectrometry*. *Talanta*. 2018;183:283-289. doi:10.1016/j.talanta.2018.02.023
2. Teledyne Leeman, *New Technical note describing the advantages of an ICP spectrometer with a wavelength range of 165 – 1100 nm*, www.teledyneleemanlabs.com/companyinfo/Press-Releases/Pages/PR-Iodine.aspx, March 2006
3. Morishige Y.; Kimura A., *Ionization Interference in Inductively Coupled Plasma-Optical Emission Spectroscopy*, SEI Technical Review Number 66, April 2008.
4. King W. D.; Nash C. A.; Taylor-Pashow K. M. L.; Hang T.; Hamm L.L.; Aleman S.E.; Fondeur F.F. *Cesium Removal Performance Comparisons of Crystalline Silicotitanate Media Batches with Savannah River Site Waste Simulant*. SRNL-STI-2019-00648, Rev 2, Savannah River National Laboratory (SRNL): Aiken, SC, 2020.
5. Juillerat C. A.; Kocevski V.; Klepov V. V.; Amoroso J. W.; Besmann T. M.; zur Loye H-C. *Structure and Stability of Alkali Gallates Structurally Reminiscent of Hollandite*. J Am Ceram Soc. 2020;00:1-12. https://doi.org/10.1111/jace.17327.
6. Taylor-Pashow K. M. L.; Nash C. A. *Summary of Expedited Results from Samples Supporting Tank Closure Cesium Removal (TCCR) Batch 3*. SRNL-STI-2020-00269, Rev 0, Savannah River National Laboratory (SRNL): Aiken, SC, 2020.

Acronyms

Ba	Barium
Cs	Cesium
CST	Crystalline Silicotitanate
DF	Dilution Factor
EIE	Easily Ionizable Elements
G/L	Gram/Liter
HNO_3	Nitric Acid
IB	Ionization Buffer
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Li	Lithium
L-PAD	Large Format Programmable Array Detector
K	Potassium
LOQ	Limit of Quantitation
MG/L	Milligram per Liter
ML	Milliliter
Na	Sodium
NaPFLiC	Sodium Peroxide Fusion/Lithium Carbonate Buffer Solution
NM	Nanometers
NonRad	Non-Radiological
UG/G	Microgram per gram
PPB	Parts Per Billion
PPM	Parts Per Million
PF	Peroxide Fusion
RAD	Radiological
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
UL	Microliter

Intellectual Property

Not Applicable.

Total Number of Post-Doctoral Researchers

Not Applicable.

Total Number of Student Researchers

Not Applicable.

External Collaborators (Universities, etc.)

Not Applicable.